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GB 2242909 A **EP 0627484 A1** **EP 0580245 A2**
EP 0552054 A1 **EP 0544492 A1** **EP 0384070 A1**

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(54) Detergent composition containing Zeolite MAP

(57) Detergent compositions are disclosed comprising a surfactant, a detergency builder comprising zeolite P having a silicon to aluminium ratio not greater than 1.33 (zeolite MAP) and a clay mineral optionally together with a clay flocculating agent. The compositions provide improved fabric colour pattern maintenance.

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TITLE: DETERGENT COMPOSITION

The present invention relates to a detergent composition and, in particular, to improvements in the detergency performance of laundry detergent compositions comprising zeolites as sequestering agents for water hardness.

Detergent compositions for fabric washing conventionally contain detergency builders which lower the concentration of calcium and magnesium water hardness ions in the wash liquor and thereby provide good detergency effect in both hard and soft water.

Conventionally, inorganic phosphates, such as sodium tripolyphosphate, have been used as builders for laundry detergents. More

recently, alkali metal aluminosilicate ion-exchangers, particularly crystalline sodium aluminosilicate zeolite A, have been proposed as replacements for the inorganic phosphates.

For example, EP 21 491A (Procter & Gamble) discloses detergent compositions containing a building system which includes zeolite A, X or P (B) or a mixture thereof. EP 384070A (Unilever) discloses specific zeolite P materials having an especially low silicon to aluminium ratio not greater than 1.33 (hereinafter referred to as zeolite MAP) and describes its use as a detergency builder. To date, however, zeolite A is the preferred aluminosilicate detergency builder in commercially available products.

It has now been found that zeolite MAP, particularly when present as small particles, such as those having a particle size of less than 1 μm, may abrade coloured patterns from printed fabrics. This problem of coloured pattern abrasion can surprisingly be solved by the inclusion of a clay mineral component together with the zeolite MAP component.

It has also been found that the use of zeolite MAP in combination with a clay mineral component results in synergistic fabric softening benefits.

A particular problem has been found with the flowability of granular compositions containing zeolite MAP. Such compositions have been found to exhibit, in certain circumstances, sticky physical characteristics which, in turn lead to poor flowability. Surprisingly, incorporation of a clay mineral compound has been found to ameliorate this problem.

Thus, the present invention provides a detergent composition comprising:

(a) a surfactant selected from anionic, nonionic, cationic, amphoteric and zwitterionic detergent-active compounds and mixtures thereof;

(b) a detergency builder comprising zeolite P having a silicon to aluminium ratio not greater than 1.33 (zeolite MAP); and

(c) a clay mineral.

According to another aspect of the invention there is provided an additive component for a detergent comprising zeolite MAP and a clay mineral. Such an additive may optionally also include a clay flocculating agent.

The detergent composition according to the invention contains, as an essential ingredient, one or more surfactants selected from anionic, nonionic, cationic, amphoteric and zwitterionic detergent-active compounds and mixtures thereof. Such surfactants are well known and described in the literature, for example, in "Surface-Active Agents and Detergents", Volumes I and II by Schwartz, Perry and Berch.

Examples of suitable anionic surfactants include alkylbenzene sulphonates, particularly sodium linear alkylbenzene sulphonates having an alkyl chain length of C_8-C_{15}; C_{12}-C_{15} primary alkyl sulphates; olefin sulphonates; alkyl xylene sulphonates and their ethoxylated analogues containing from 0.25 to 6 moles of ethylene oxide per mole of alkyl sulphate; dialkyl sulphosuccinates; and fatty acid ester sulphonates. Sodium salts are generally preferred.

Examples of suitable nonionic surfactants include alkoxylated adducts of fatty alcohols containing an average of from 3 to 10 alkylene oxide groups

per molecule.

Preferred alkoxylated adducts of fatty alcohols containing an average of less than 5 alkylene oxide groups per molecule, for example less than 4 alkylene oxide groups per molecule e.g. 3.5 and usefully 3 alkylene oxide groups per molecule or less and usefully also greater than 0.5, or 1, or 2 alkylene oxide groups per molecule.

Alkylene oxide adducts of fatty alcohols useful as hydrophobic alkoxylated nonionic surfactants in the present invention can suitably be chosen from those of the general formula:

$$R\text{-}O\text{-}(C_nH_{2n}O)_yH$$

wherein R is an alkyl or alkenyl group having at least 10 carbon atoms, most preferably from 10 to 22 carbon atoms, y is preferably from about 0.5 to about 3.5 and n is 2 or 3.

Preferred nonionic surfactants include primary C_{11}-C_{15} aliphatic alcohols condensed with an average of no more than five ethylene oxide groups per mole of alcohol, having an ethylene oxide content of less than 50% by weight.

A particularly preferred aliphatic alcohol ethoxylate is a primary alcohol having an average of 12 to 15 carbon atoms in the alkyl chain condensed with an average of three ethoxy groups per mole of alcohol.

Specific examples of suitable alkoxylated adducts of fatty alcohols are Synperonic A3 (ex ICI), which is a C_{13}-C_{15} alcohol with about three ethylene

oxide groups per molecule and Empilan KB3 (ex Marchon), which is lauric alcohol 3EO.

Another class of nonionic surfactants comprises alkyl polyglucoside compounds of general formula

$$RO(C_nH_{2n}O)_tZ_x$$

wherein Z is a moiety derived from glucose; R is a saturated hydrophobic alkyl group that contains from 12 to 18 carbon atoms; t is from 0 to 10 and n is 2 or 3; x is from 1.1 to 4, the compounds including less than 10% unreacted fatty alcohol and less than 50% short chain alkyl polyglucosides. Compounds of this type and their use in detergent compositions are disclosed in EP-B 0070074, 0070077, 0075996 and 0094118.

Where the composition comprises an aliphatic alcohol ethoxylate as the hydrophobic nonionic surfactant it is present in an amount of at least 1 wt.%, preferably from 1 wt.% to 10 wt.% and more preferably 1 wt.% to 6 wt.% of the composition.

The detergent composition of the invention generally contains a detergent surfactant in a range of from 1 to 60 wt.%, preferably 4 to 40 wt.% and most preferably from 7 to 25 wt.% of the composition.

According to the present invention the detergency builder system is based on zeolite MAP, optionally in conjunction with one or more supplementary builders. The amount of zeolite MAP employed may range, for example, from 1 to 60 wt.%, more preferably from 10 to 40 wt.%.

Zeolite MAP is described in EP 384070A (Unilever). It is defined as an alkali metal alumino-silicate of the zeolite P type having a silicon to

aluminium ratio not greater than 1.33, preferably within the range from 0.9 to 1.33 and more preferably within the range of from 0.9 to 1.2.

Of particular interest is zeolite MAP having a silicon to aluminium ratio not greater than 1.15 and, more particularly, not greater than 1.07.

Zeolite P having a Si:Al ratio of 1.33 or less

may be prepared by the following steps:

(i) mixing together a sodium aluminate having a mole ratio $Na_2O:Al_2O_3$ within the range of from 1.4 to 2.0 and a sodium silicate having a mole ratio $SiO_2:Na_2O$ within the range of from 0.8 to 3.4 with vigorous stirring at a temperature within the range of from 25°C to boiling point usually 95°C, to give a gel having the following composition;

Al_2O_3: (1.75-3.5) SiO_2 : (2.3-7.5) Na_2O :P (80-450)H_2O;

(ii) ageing the gel composition for 0.5 to 10 hours, preferably 2 to 5 hours, at a temperature within the range of from 70°C to boiling point, usually to 95°C, with sufficient stirring to maintain any solids present in suspension;

(iii) separating the crystalline sodium aluminosilicate thus formed, washing to a pH within the range of from 10 to 12.5, and drying, preferably at a temperature not exceeding 150°C, to a moisture content of not less than 5 wt.%.

Preferred drying methods are spray-drying and flash drying. It appears that oven drying at too high a temperature may adversely affect the calcium binding capacity of the product under certain circumstances.

Commercial sodium metasilicate pentahydrate dissolved in water and commercial sodium silicate solution (waterglass) are both suitable silica

sources for the production of zeolite P in accordance with the invention. The reactants may be added together in any order either rapidly or slowly. Rapid addition at ambient temperature, and slow addition at elevated temperature (90-95°C) both give the desired product.

Vigorous stirring of the gel during the addition of the reactants, and at least moderate stirring during the subsequent ageing step, however, appear to be essential for the formation of pure zeolite P. In the absence of stirring, various mixtures of crystalline and amorphous materials may be obtained.

Zeolite MAP generally has a calcium binding capacity of at least 150 mg CaO per g of anhydrous aluminosilcate, as measured by the standard method described in GB 1473201 (Henkel). The calcium binding capacity is normally 160 mg CaO/g and may be as high 170 mg CaO/g.

Although zeolite MAP like other zeolites contains water of hydration, for the purposes of the present invention amounts and percentages of zeolite are expressed in terms of the notional anhydrous material.

The amount of water present in hydrated zeolite MAP at ambient temperature and humidity is generally about 20 wt.%.

A preferred zeolite MAP for use according to the present invention has a d_{50} of from 1.0 to 5.0 micrometres, for example 2.25 to 5 micrometres, more particularly 2.75 to 5 micrometres. The quantity "d_{50}" indicates that 50 wt.% of the particles have a diameter smaller than that figure.

According to one embodiment of the invention the zeolite MAP detergent builder is in powder form.

For convenience in handling, however, the material may be granulated

by conventional techniques such as spray drying or by a non-tower method such as an agglomeration method to form larger particles.

The detergent composition according to the invention comprises, as an essential component, a clay mineral.

The clay mineral is preferably present in the detergent composition according to the invention in a proportion of from 0.05% to 40%, more preferably from 0.5% to 30%, most preferably from 2% to 20% by weight of the composition.

The weight ratio of Zeolite MAP to clay mineral is preferably from 1:10 to 10:1, more preferably from 1:5 to 5:1, most preferably from 1:3 to 3:1.

The clay mineral is preferably a smectite clay. Smectite clays are disclosed in the US Patents No.s 3,862,058 3,948,790, 3,954,632 and 4,062,647 and European Patents No.s EP-A-299,575 and EP-A-313,146 all in the name of the Procter and Gamble Company.

The term smectite clays herein includes both the clays in which aluminium oxide is present in a silicate lattice and the clays in which magnesium oxide is present in a silicate lattice. Typical smectite clay compounds include the compounds having the general formula $Al_2(Si_2O_5)_2(OH)_2.nH_2O$ and the compounds having the general formula $Mg_3(Si_2O_5)_2(OH)_2.nH_2O$. Smectite clays tend to adopt an expandable three layer structure.

Specific examples of suitable smectite clays include those selected from the classes of the montmorillonites, hectorites, nontronites, saponites and

sauconites, particularly those having an alkali or alkaline earth metal ion within the crystal lattice structure. Sodium or calcium montmorillonite are particularly preferred.

Suitable smectite clays, particularly montmorillonites, are sold by various suppliers including English China Clays, Laviosa, Georgia Kaolin and Colin Stewart Minerals.

Clays for use herein preferably have a largest particle dimension of from 0.01 μm to 800 μm, more preferably from 1 μm to 400 μm, most preferably from 5 μm to 200 μm.

Particles of the clay mineral may be included as components of agglomerate particles containing other detergent compounds. Where present as such components, the term "largest particle dimension" of the clay mineral refers to the largest dimension of the clay mineral component as such, and not to the agglomerated particle as a whole.

Substitution of small cations, such as protons, sodium ions, potassium ions, magnesium ions and calcium ions, and of certain organic molecules including those having positively charged functional groups can typically take place within the crystal lattice structure of the smectite clays. A clay may be chosen for its ability to preferentially absorb one cation type, such ability being assessed by measurements of relative ion exchange capacity. The smectite clays suitable herein typically have a cation exchange capacity of at least 50 meq/100g. U.S. Patent No. 3,954,632 describes a method for measurement of cation exchange capacity.

The crystal lattice structure of the clay mineral may have, in a

preferred embodiment. a cationic fabric softening agent substituted therein. Such substituted clays have been termed 'hydrophobically activated' clays. The cationic fabric softening agents are typically present at a weight ratio, cationic fabric softening agent to clay, of from 1:200 to 1:10, preferably from 1:100 to 1:20. Suitable cationic fabric softening agents include the water insoluble tertiary amines or dilong chain amide materials as disclosed in GB-A-1 514 276 and EP-B-0 011 340.

A preferred commercially available "hydrophobically activated" clay is a bentonite clay containing approximately 40% by weight of a dimethyl ditallow quaternary ammonium salt sold under the tradename Claytone EM by English China Clays International.

The compositions of the invention preferably contain a clay flocculating agent, preferably present at a level of from 0.005% to 10%, more preferably from 0.05% to 5%, most preferably from 0.1% to 2% by weight of the composition.

The weight ratio of clay mineral to clay flocculating agent is preferably from 300: 1 to 1:1, more preferably from 80:1 to 10:1, most preferably from 60:1 to 20:1.

The clay flocculating agent functions such as to bring together the particles of clay in the wash solution and hence to aid their deposition onto the surface of the fabrics in the wash. This functional requirement is hence different from that of clay dispersant compounds which are commonly added to laundry detergent compositions to aid the removal of clay soils from fabrics and enable their dispersion within the wash solution.

Preferred as clay flocculating agents herein are organic polymeric materials having an average molecular weight of from 100.000 to 10.000.000, preferably from 150.000 to 5.000.000, more preferably from 200.000 to 2.000.000.

Suitable organic polymeric materials comprise homopolymers or copolymers containing monomeric units selected from alkylene oxide, particularly ethylene oxide, acrylamide, acrylic acid, vinyl alcohol, vinyl pyrrolidone, and ethylene imine. Homopolymers of ethylene oxide, acrylamide and acrylic acid are preferred.

European Patents No.s EP-A-299,575 and EP-A-313,146 in the name of the Procter and Gamble Company describe preferred organic polymeric clay flocculating agents for use herein.

Inorganic clay flocculating agents are also suitable herein, typical examples of which include lime and alum.

In the detergent compositions according to the invention, the detergency builder can be zeolite MAP alone or a combination of zeolite MAP with an organic or inorganic cobuilder.

Suitable organic cobuilders can be monomeric or polymeric carboxylates such as citrates or polymers of acrylic, methacrylic and/or maleic acids in neutralised form. Suitable inorganic cobuilders include carbonates and amorphous and crystalline lamellar sodium silicates.

Suitable crystalline lamellar silicates have the composition:

$$NaMSi_xO_{2x+1} \cdot yH_2O$$

where M is sodium or hydrogen, preferably sodium; x is a number from 1.9 to 4; and y is a number from 0 to 20. Such materials are described in US Patents No. 4664839; No. 4728443 and No. 4820439 (Hoechst AG). Especially preferred are compounds in which x = 2 and y = O. The synthetic material is commercially available from Hoechst AG as δ-$Na_2Si_2O_5$ (SKS6) and is described in US Patent No. 4664830.

The total amount of detergency builder in the composition preferably ranges from 1 to 80 wt.%, more preferably from 5 to 60 wt% and most preferably from 10 to 45 wt.%.

Detergent compositions according to the invention may also suitably contain a bleach system. This preferably comprises one or more peroxy bleach compounds, for example, inorganic persalts or organic peroxyacids, which may be employed in conjunction with bleach precursors to improve bleaching action at low temperatures.

The bleach system preferably comprises a peroxy bleach compound, preferably an inorganic persalt, optionally in conjunction with a precursor. Suitable persalts include sodium perborate monohydrate and tetrahydrate, with sodium percarbonate being most preferred.

Preferred bleach precursors are peracetic acid precursors, such as tetraacetylethylene diamine (TAED); and peroxybenzoic acid precursors such as sodium benzoyloxybenzene sulphonate (BOBS) and benzoyl caprolactam (BZCL).

Other materials which may be present in the detergent compositions of the invention include, for example, fluorescers, antiredeposition agents,

inorganic salts such as sodium sulphate, enzymes, lather control agents, fabric softening agents, pigments, perfumes and coloured speckles.

The detergent compositons of the invention are in one preferred aspect in solid form. Preferred forms include granules, powders and tablets. Granular compositions are especially preferred.

The detergent compositions of the invention may be prepared by any suitable method, for example by any tower (spray-drying) or non-tower process, including agglomeration.

In processes based around a spray-drying tower, a base powder is first prepared by spray-drying a slurry and then other components unsuitable for processing via the slurry can be sprayed on or admixed (postdosed).

The zeolite MAP is suitable for inclusion in the slurry, although it may be advantageous for processing reasons for part of the zeolite MAP to be incorporated post-tower. The lamellar silicate, where this is employed, is also incorporated via a non-tower process and is preferably postdosed.

Alternatively, granular detergent compositions in accordance with the invention may be prepared by wholly non-tower processes such as granulation.

The granular detergent compositions of the invention may be prepared to any suitable bulk density. The compositions preferably have a bulk density of at least 400 g/l preferably at least 550 g/l, most preferably at least 700 g/l and, with particular preference at least 800 g/l.

The benefits of the present invention are particularly evident in powders of high bulk density, for example, of 700 g/l or above. Such powders may be prepared either by post-tower densification of spray-dried

powder, or by wholly non-tower methods such as dry mixing and agglomeration; in both cases a high-speed mixer/granulator may advantageously be used. Processes using high-speed mixer/granulators are disclosed, for example, in EP340 013A, EP 367 339A, EP 390 251A and EP 420 317A (Unilever).

The detergent composition according to the invention generally has a pH (as measured with a 1% solution in distilled water) of above 9.0, preferably above 9.5 and with particular preference about 10.

According to a further aspect, the invention provides use of a composition comprising zeolite MAP and clay, optionally in combination with a clay flocculating agent as an additive for a detergent composition.

Illustrative compositions according to the present invention are presented in the following Examples.

The following abbreviations have been used in the Tables:

XYAS	:	Sodium C_{1X} - C_{1Y} alkyl sulfate
25EY	:	A C_{12-15} predominantly linear primary alcohol condensed with an average of Y moles of ethylene oxide
XYEZ	:	A C_{1x} - C_{1y} predominantly linear primary alcohol condensed with an average of Z moles of ethylene oxide
XYEZS	:	C_{1X} - C_{1Y} sodium alkyl sulfate condensed with an average of Z moles of ethylene oxide per mole
TFAA	:	C_{16}-C_{18} alkyl N-methyl glucamide.
Silicate	:	Amorphous Sodium Silicate (SiO_2:Na_2O ratio = 2.0)

NaSKS-6	:	Crystalline layered silicate of formula δ-$Na_2Si_2O_5$
Carbonate	:	Anhydrous sodium carbonate
Polycarboxylate	:	Copolymer of 1:4 maleic/acrylic acid, average molecular weight about 80,000
Citrate	:	Tri-sodium citrate dihydrate
Percarbonate	:	Anhydrous sodium percarbonate bleach coated with a coating of sodium silicate (Si_2O:Na_2O ratio = 2:1) at a weight ratio of percarbonate to sodium silicate of 39:1
TAED	:	Tetraacetylethylenediamine particle formed by agglomerating TAED with citric acid and polyethylene glycol (PEG) of Mw=4,000 with a weight ratio of components of TAED:citric acid:PEG of 75:10:15, coated with an external coating of citric acid at a weight ratio of agglomerate: citric acid coating of 95:5.
Protease	:	Proteolytic enzyme sold under the tradename Savinase by Novo Industries A/S with an activity of 13 KNPU/g.
Cellulase	:	Cellulosic enzyme sold by Novo Industries A/S with an activity of 1000 CEVU/g
Lipase	:	Lipolytic enzyme sold under the tradename Lipolase by Novo Industries A/S with an activity of 165 KLU/g
CMC	:	Sodium carboxymethyl cellulose
HEDP	:	1,1-hydroxyethane diphosphonic acid
EDDS	:	Ethylenediamine -N, N'- disuccinic acid, [S,S] isomer in the form of the sodium salt.
PVNO	:	Poly (4-vinylpyridine)-N-oxide copolymer of vinylimidazole and vinylpyrrolidone having an average molecular weight of 10,000.

Clay		Calcium montmorillonite
Granular Suds Suppressor	:	12% Silicone/silica, 18% stearyl alcohol, 70% starch in granular form

Example 1

The following granular laundry detergent compositions of bulk density of about 750g/litre A to D were prepared in accord with the invention:

	A	B	C	D
45AS/25AS (3:1)	9.1	9.1	9.1	9.1
35AE3S	2.3	2.3	2.3	2.3
24E5	4.5	4.5	4.5	4.5
TFAA	2.0	2.0	2.0	2.0
Zeolite MAP	10.2	10.2	10.2	7.2
Na SKS-6/citric acid (79:21)	10.6	10.6	10.6	10.6
Carbonate	7.6	7.6	7.6	7.6
TAED	6.3	5.0	5.0	3.75
Percarbonate	22.5	22.5	22.5	22.5
Clay	12.0	12.0	12.0	15.0
DETPMP	0.5	0.8	-	-
EDDS	-	-	0.3	0.75
Protease	0.55	1.27	0.55	1.27
Lipase	0.15	0.15	0.15	0.15
Cellulase	0.28	0.28	0.28	0.28

Polycarboxylate	3.1	3.1	3.1	3.1
CMC	0.4	0.4	0.4	0.4
PVNO	0.03	0.03	0.03	0.03
Granular suds suppressor	1.5	1.5	1.5	1.5
Minors/misc to 100%				

Example 2

The following granular laundry detergent compositions of bulk density of about 750 g/litre E to H were prepared in accord with the invention:

	E	F	G	H
45AS/25AS (3:1)	9.1	9.1	9.1	9.1
35AE3S	2.3	2.3	2.3	2.3
24E5	4.5	4.5	4.5	4.5
TFAA	2.0	2.0	2.0	2.0
Zeolite MAP	10.2	10.2	10.2	10.2
Na SKS-6/citric acid (79:21)	10.6	10.6	10.6	10.6
Carbonate	7.6	7.6	7.6	7.6
TAED	7.3	7.3	2.3	2.3
Percarbonate	22.5	22.5	22.5	22.5
Clay	6.0	12.0	9.0	12.0
DETPMP	0.5	0.5	-	-
EDDS	-	-	0.3	0.3
Protease	0.55	0.55	0.55	0.55
Lipase	0.15	0.15	0.15	0.15
Cellulase	0.28	0.28	0.28	0.28
Polycarboxylate	3.1	3.1	3.1	3.1
CMC	0.4	0.4	0.4	0.4

PVNO	0.03	0.03	0.03	0.03
Granular suds suppressor	1.5	1.5	1.5	1.5
Minors/misc to 100%				

CLAIMS:

1. A detergent composition comprising:

(a) a surfactant selected from anionic, nonionic, cationic, amphoteric and zwitterionic detergent-active compounds and mixtures thereof;

(b) a detergency builder comprising zeolite P having a silicon to aluminium ratio not greater than 1.33 (zeolite MAP); and

(c) a clay mineral.

2. A detergent composition according to claim 1 which further comprises a clay flocculating agent.

3. A detergent composition according to claim 1 or 2 wherein the zeolite MAP has a silicon to aluminium ratio not greater than 1.07.

4. A detergent composition according to any one of claims 1 to 3, wherein the zeolite MAP has a particle size d_{50} of 1 to 5 micrometres.

5. A detergent composition according to any one of claims 1 to 4 which comprises from 1 to 60 wt% of the zeolite MAP.

6. A detergent composition according to claim 1 which comprises from 10 to 40 wt% of the zeolite MAP.

7. A detergent composition according to any one of claims 1 to 6, wherein the detergency builder (b) comprises zeolite MAP together with a cobuilder selected from monomeric and polymeric carboxylates; polymers of acrylic, methacrylic and/or maleic acids in neutralised form; carbonates and amorphous and crystalline lamellar sodium silicates.

8. A detergent composition according to claim 7, wherein the cobuilder is a lamellar sodium silicate of the composition:

$$Na\ M\ Si_xO_{2x+1}\ .\ yH_2O$$

wherein M is sodium or hydrogen, x is a number from 1.9 to 4 and y is a number from 0 to 20.

9. A detergent composition according to any one of claims 1 to 8, which has a pH (as measured with a 1% solution in distilled water) of above 9.

10. A detergent composition according to claim 1 wherein the clay mineral is a smectite clay.

11. A detergent composition according to any of claims 1 to 10, which comprises from 2% to 20% by weight of the clay mineral based on the composition.

12. A detergent composition according to any of claims 1 to 11, wherein the weight ratio of the zeolite MAP to the clay mineral is 1:3 to 3:1.

13. A detergent composition according to any of claims 2 to 12, wherein the clay flocculating agent is an organic polymeric material having an average molecular weight of 100.000 to 10.000.000.

14. A detergent composition according to any of claims 1 to 13, which is formulated as a granular composition.

15. An additive component for a detergent composition comprising zeolite MAP, a clay mineral and, optionally, a clay flocculating agent.

The Patent Office

Application No: GB 9502321.4 **Examiner:** John Wilson
Claims searched: 1-15 **Date of search:** 26 May 1995

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.N): C5D[DEX DHC]

Int Cl (Ed.6): C11D 3/08 3/12 3/14

Other: Online: EDOC, WPI

Documents considered to be relevant:

Category	Identity of document and relevant passage		Relevant to claims
Y	GB2242909A	ECC International - whole document	1 at least
Y	EP0627484A1	Procter & Gamble - whole document	1 at least
Y	EP0580245A2	Colgate-Palmolive - whole document	1 at least
Y	EP0552054A1	Unilever - whole document	1 at least
Y	EP0544492A1	Unilever - whole document	1 at least
Y	EP0384070A1	Unilever - whole document	1 at least

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.

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